

PATENT ABSTRACTS OF JAPAN

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(21)Application number : 11-226121 (71)Applicant: HITACHI MAXELL LTD

(22)Date of filing : 10.08.1999 (72)Inventor : SHINODA NAOKI

(54) NONAQUEOUS ELECTROLYTE AND NONAQUEOUS ELECTROLYTE SECONDARY BATTERY USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery capable of having at least one electrode potential of 4.5 V based on lithium, by providing nonaqueous electrolyte stable at 5 V or more on the surface of a carbon material.

SOLUTION: A nonaqueous electrolyte containing at least two of ether containing fluorine, unsaturated ether or unsaturated ester in the volume ratio of 5% or more for each is formed. A nonaqueous electrolyte containing at least two of ether containing fluorine, unsaturated ether or unsaturated ester, and other electrolyte solvent is formed. In this case, the nonaqueous electrolyte contains the enter with fluorine, the unsaturated ether or unsaturated ester mentioned above in the volume ratio of 5% or more for each, and uses the other electrolyte solvent 85% of which is a solvent stable at 5 V or more on the surface of a triester phosphate and/or a carbon material.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the nonaqueous electrolyte rechargeable battery which can be high-voltage-ized in more detail using the nonaqueous electrolyte and it which can bear the high voltage about the nonaqueous electrolyte rechargeable battery which used nonaqueous electrolyte and it.

PRIOR ART

[Description of the Prior Art] Production has expanded rapidly the nonaqueous electrolyte rechargeable battery represented by the lithium secondary battery in recent years from it being high capacity and their being a high voltage and a high energy consistency.

EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, in this invention, stable nonaqueous electrolyte can be offered more than 5V on a carbon material front face, and the nonaqueous electrolyte

rechargeable battery from which one [at least] electrode potential can be set to 4.5V on lithium criteria by it can be offered now.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Although the further high capacity-ization is called for also in this nonaqueous electrolyte rechargeable battery along with the spread of small pocket devices etc., positive active material is changed into 5V class from the 4V class conventional thing as an idea of the technique for it, and the attempt which is going to aim at the capacity rise of the power base by raising cell voltage is made.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the nonaqueous electrolyte rechargeable battery which can be high-voltage-ized in more detail using the nonaqueous electrolyte and it which can bear the high voltage about the nonaqueous electrolyte rechargeable battery which used nonaqueous electrolyte and it.

[0002]

[Description of the Prior Art] Production has expanded rapidly the nonaqueous electrolyte rechargeable battery represented by the lithium secondary battery in recent years from it being high capacity and their being a high voltage and a high energy consistency.

[0003]

[Problem(s) to be Solved by the Invention] Although the further high capacity-ization is called for also in this nonaqueous electrolyte rechargeable battery along with the spread of small pocket devices etc., positive active material is changed into 5V class from the 4V class conventional thing as an idea of the technique for it, and the attempt which is going to aim at the capacity rise of the power base by raising cell voltage is made.

[0004] However, although used as a solvent of the nonaqueous electrolyte for current nonaqueous electrolyte rechargeable batteries (it abbreviates to the "electrolytic solution" hereafter except when a cell is expressed), if cell voltage becomes more than 5V, oxidative degradation of most will be carried out on carbon material front faces, such as a graphite currently used as an electric conduction assistant of a positive electrode. Therefore, for utilization of a 5V class cell, it is required to use the electrolytic-solution solvent which is hard to disassemble more than 5V.

[0005]

[Means for Solving the Problem] This invention is made as a result of [which should solve the above-mentioned technical problem] inquiring wholeheartedly. As an electrolytic-solution solvent By making at least two, the fluorine-containing ether, the ether of partial saturation, or partial saturation ester, contain 5% or more by the volume ratio, respectively It hardly decomposes on a carbon material front face more than 5V, or even if it decomposes first, it stabilizes immediately, and it finds out that the electrolytic solution which is not disassembled at all is obtained after it.

[0006] That is, this invention person found out that the electrolytic solution with which at least two, the fluorine-containing ether, the partial saturation ether, or partial saturation ester, are contained 5% or more by the volume ratio, respectively could stabilize and use it also on the

carbon material front face beyond 5V. In the conventional electrolytic solution, if an electrical potential difference rises to 5V, decomposition will be continuously continued on a carbon material front face, but in the electrolytic solution of this invention, although some decomposition current flows first, a decomposition reaction completes and is stable in a very early phase, and decomposition is not caused after it to 6.5V at least.

[Means for Solving the Problem] This invention is made as a result of [which should solve the above-mentioned technical problem] inquiring wholeheartedly. As an electrolytic-solution solvent By making at least two, the fluorine-containing ether, the ether of partial saturation, or partial saturation ester, contain 5% or more by the volume ratio, respectively It hardly decomposes on a carbon material front face more than 5V, or even if it decomposes first, it stabilizes immediately, and it finds out that the electrolytic solution which is not disassembled at all is obtained after it. [0007]

[Embodiment of the Invention] As the fluorine-containing ether used in this invention, what has the high oxidation resistance of itself is desirable, and since oxidation resistance is also high, 30% or more of the rate of fluorination is so desirable that the rate of fluorination (substitutional rate to the fluorine of hydrogen) is high, and 55% or more is more desirable. Moreover, the field of a cell property to the molecular structure has the desirable shape of a chain, and is desirable. [of the shape especially of a straight chain] furthermore, a straight chain-like case -- at least 1 end -CHF₂ it is -- things are desirable. 5% or more of the ratio in the inside of the electrolytic-solution solvent of the fluorine-containing ether is required of a volume ratio, is desirable for acquiring sufficient effectiveness, is more desirable, and is still more desirable. [30% or more of] [20% or more of] [10% or more of] However, from the field of a cell property, 80% or less of the ratio in the inside of the electrolytic-solution solvent of the fluorine-containing ether is desirable at a volume ratio.

[0008] As the partial saturation ether or partial saturation ester, for example, vinylene carbonate and its derivative (for example, dimethyl-1, 3-dioxol-2-one) are mentioned as a suitable thing, 5% or more is required of a volume ratio, and 10% or more of the ratio in the inside of an electrolytic-solution solvent is desirable for acquiring sufficient effectiveness. However, from the field of a cell property, 60% or less of the ratio in the inside of the partial saturation ether or the electrolytic-solution solvent of partial saturation ester is desirable at a volume ratio, and is more desirable. [30% or less of]

[0009] Furthermore, although the solvent of arbitration can be mixed and used besides the two above-mentioned kinds of solvents, 85% or more must be a solvent also with stable 5V on trialkyl phosphate and/or a carbon material front face in the volume ratio in such a solvent. As the above-mentioned trialkyl phosphate, phosphoric-acid trialkyl, such as trimethyl phosphate and phosphoric-acid triethyl, is mentioned. Since trialkyl phosphate will be more promptly stabilized if it mixes with the two above-mentioned kinds of solvents and it is used, it is desirable in an electrolytic-solution solvent at a volume ratio, and it is more desirable. [10% or more of] [5% or more of] However, from the field of a cell property, 80% or less of the ratio in the electrolytic-solution solvent of the above-mentioned trialkyl phosphate is desirable at a volume ratio, and is still more desirable. [40% or less of] Moreover, as a stable solvent, the fluorinated ether (the same kind as the fluorine-containing ether which is the indispensable configuration solvent of this invention is also available for this), the ester which were fluorinated, and the carbonate which were fluorinated are independently mentioned more than 5V on a carbon material front face. In addition, with stability, it means that decomposition quantity of electricity

not more than 5V is 0.05 or less mFs per electrode unit area in the same withstand voltage test as having been shown in the example of this invention more than 5V here, and, as for a stable thing, more than 5.5V is desirable under these conditions in this invention.

[0010] As an electrolyte of the electrolytic solution, for example LiClO₄ and LiPF₆, LiBF₄, LiAsF₆, LiSbF₆, and LiCF₃SO₃, LiC₄F₉SO₃, LiCF₃CO₂, and Li₂C₂F₄·2(SO₃), LiN(CF₃SO₂)₂, LiC(CF₃SO₂)₃, LiC_nF_{2n+1}SO₃(n>=2), and LiN(RfOSO₂)₂ [-- here -- Rf -- fluoro alkyl group etc. -- independent -- or, although two or more sorts are mixed and it is used It is especially LiPF₆. A with a carbon numbers of two or more organic fluoride Li salt etc. is desirable. Although especially the concentration of the electrolyte in the electrolytic solution is not limited, since its safety will improve more if concentration is made into the numerousness of 0.6 or more mol/l, it is desirable, and its 0.8 or more mol/l is more desirable. Moreover, it is more desirable when fewer than desirable 1.6 mol/l, since viscosity will become low if fewer than 2.0 mol/l. Although the electrolytic solution is prepared by dissolving these electrolytes into an electrolytic-solution solvent, it can be considered that the volume of the electrolyte in the electrolytic solution is very small, the volume of the electrolytic solution is substantially [as the volume of an electrolytic-solution solvent] the same, and the volume occupied in electrolytic-solution solvents, such as the above-mentioned fluorine-containing ether, the partial saturation ether or partial saturation ester, and trialkyl phosphate, is the same as the volume which they occupy in the electrolytic solution on parenchyma.

[0011] The anything which operates by 4.5-6V as positive active material in this invention, although it is good, it is LiMn₂O₄, for example. 5V system lithium manganic acid ghost which permuted nickel, Cr, Fe, etc. is mentioned as a suitable thing. Especially since what carried out nickel permutation is excellent in the cycle property etc. also in these, it is desirable. Furthermore, although a carbon material is usually used for a positive electrode as an electric conduction assistant, since this invention controls disassembly of the electrolytic solution on the carbon material of an electric conduction assistant, if it is applied to the positive electrode which used the carbon material as an electric conduction assistant, effectiveness will show up in improvement in a cycle life etc. Although a conductive high graphite ingredient is desirable as a carbon material as an electric conduction assistant, especially since a cell property will improve into a graphite ingredient if minute amount concomitant use of the low crystal ingredients, such as carbon black, is carried out, it is desirable. In order to secure a capacity consistency as an amount of an electric conduction assistant, 20% or less is desirable at a weight ratio in a positive-electrode ingredient (that is, it does not consist of positive active material, an electric conduction assistant, a binder, etc., and neither a charge collector nor a tab is included), 10% or less is still more desirable, but in order to secure conductivity, 5% or more is desirable. Moreover, since the graphite ingredient which covered the front face with the low crystal carbon material, and made it amorphous by CVD (chemistry gaseous-phase method) etc. especially as the above-mentioned graphite ingredient is more promptly stable with the electrolytic solution, it is desirable. It is [in / with such a graphite ingredient made amorphous / a Raman spectrum] desirable that the peak intensity ratio (I₁₃₆₀/I₁₆₀₀) of 1360cm⁻¹ and 1600cm⁻¹ is 0.4 or more.

[0012] A positive electrode responds for example, to the above-mentioned positive active material at the need. Above electric conduction assistants and polyvinylidene fluorides, A mixture is prepared. binders, such as polytetrafluoroethylene, -- adding -- mixing -- a positive electrode -- Use a content paste as the positive-electrode charge collector which consists of a metallic foil etc. with **, and it dries and compresses. a solvent distributes it -- making -- a paste -- carrying out (a

binder being mixed with positive active material etc. after making it dissolve in a solvent beforehand) -- the positive electrode -- a mixture -- It is produced by forming a positive-electrode binder layer in some positive-electrode charge collectors [at least]. However, the production approach of a positive electrode is good by other approaches, without being restricted to the approach of the above-mentioned instantiation.

[0013] As an ingredient used for a negative electrode, that what is necessary is just a dope and the thing which can be dedoped about a lithium ion, in this invention, although a dope and the matter which can be dedoped are called a negative-electrode active material for such a lithium ion, as such a negative-electrode active material, what is necessary is just carbon compounds, such as a graphite, pyrolytic carbon, corks, glassy carbon, a baking object of an organic high molecular compound, a meso carbon micro bead, a carbon fiber, and activated carbon. Moreover, compounds, such as an oxide which can carry out the charge and discharge also of alloys, such as Si, Sn, and In, or the low voltage near Li, have some which have a high capacity compared with a carbon material, and they are desirable as a negative-electrode active material.

[0014] A negative electrode adds the same electric conduction assistant, same binder, etc. as a case of a positive electrode to for example, the above-mentioned negative-electrode active material if needed. Prepare a mixture, make a solvent distribute it and it is made a paste (since it is made to dissolve in a solvent beforehand, a binder may be mixed with a negative-electrode active material etc.). mixing -- a negative electrode -- the negative electrode -- a mixture -- a content paste is used as the negative-electrode charge collector which consists of copper foil etc. with **, is dried and compressed into it, and it is produced by forming a negative-electrode binder layer in some negative-electrode charge collectors [at least]. However, the production approach of a negative electrode is good by other approaches, without being restricted to the approach of the above-mentioned instantiation.

[0015] Although foils, such as aluminum, copper, nickel, and stainless steel, the thing which made those metals reticulated are used, for example as the above-mentioned positive-electrode charge collector or a negative-electrode charge collector, especially as a positive-electrode charge collector, aluminium foil is suitable, and copper foil is suitable especially as a negative-electrode charge collector.

[0016] Especially as a separator, although not limited, what reinforcement comes out enough and can moreover hold many electrolytic solutions is desirable, and a microporous film, a nonwoven fabric, etc. of the product [hole density] made from the copolymer of 30 - 70% of product made from polyethylene, the product made from polypropylene, ethylene, and a propylene have such a viewpoint to desirable thickness at 10-50 micrometers.

[Example] Below, an example is given and this invention is explained more concretely. However, this invention is not limited only to those examples.

[0017] 1, 1 and 2 as the example 1 fluorine-containing ether, 2-tetrafluoro ethyl - 2, 2, 3, and 3-tetrafluoro propyl ether (HCF₂ CF₂ CH₂ OCF₂ CF₂ H), the ether of partial saturation, or the vinylene carbonate as ester is mixed by the volume ratio 6:4, and it is LiPF₆ to this mixed solvent. 1.0 mols /were dissolved. and the electrolytic solution was prepared.

[0018] this -- another -- a scale-like graphite [Raman spectrum -- setting -- the peak intensity ratio (I₁₃₆₀/I₁₆₀₀) of 1360cm⁻¹ and 1600cm⁻¹ -- scale-like graphite] not more than =0.1 and the solution made to dissolve polyvinylidene fluoride in N-methyl pyrrolidone were mixed, and the paste was prepared. this mixture -- after having made it with ** one side of the positive-electrode charge collector which consists of aluminium foil with a thickness of 20 micrometers, drying on it

and pressing a paste into homogeneity with a roller press machine at it, it cut on the 1cmx1cm square, the lead object was welded to that positive-electrode charge collector, and the trial pole for withstand voltage tests was produced. Using this trial pole and the counter electrode of the lithium foil, the 4ml of the above-mentioned specific electrolytic solutions was poured in, and the test cell was assembled.

[0019] the scale-like graphite [Raman spectrum which replaced with the scale-like graphite in example 2 example 1, and made the front face amorphous with the CVD method -- setting -- the peak intensity ratio (I1360/I1600) of 1360cm⁻¹ and 1600cm⁻¹ -- the test cell was assembled like the example 1 except having used scale-like graphitel of =0.6.

[0020] 1, 1 and 2 as the example 3 fluorine-containing ether, 2-tetrafluoro ethyl - 2, 2, 3, and 3-tetrafluoro propyl ether (HCF₂ CF₂ CH₂ OCF₂ CF₂ H), The test cell was assembled like the example 1 except having used the solvent which mixed the ether of partial saturation or the dimethyl -1 as ester, 3-JIOKISORU-2-ON, and the trimethyl phosphate as trialkyl phosphate by the volume ratio 6:3:1 as an electrolytic-solution solvent.

[0021] The test cell was assembled like the example 1 except having used example of comparison 1 propylene-carbonate 100% as an electrolytic-solution solvent.

[0022] The test cell was assembled like the example 1 except having used example of comparison 2 vinylene-carbonate 100% as an electrolytic-solution solvent.

[0023] The examples 31, 1, and 2 of a comparison, 2-tetrafluoro ethyl - The test cell was assembled like the example 1 except having used the mixed solvent of the volume ratio 6:3:1 of 2, 2, 3, and 3-tetrafluoro propyl ether, propylene carbonate, and vinylene carbonate as an electrolytic-solution solvent.

[0024] [Electrolytic-solution withstand voltage test] The seal of approval of the electrical potential difference was carried out to the test cell of the above-mentioned examples 1-3 and the examples 1-3 of a comparison to 6.5V by the constant current of 50microA, and the amount of decomposition of the electrolytic solution was investigated. Consumption quantity of electricity according [before resulting in 6.5V, decomposition starts, and] to decomposition is 0.15 mF/cm². Even if reached, when there was no sign (that is, decomposition will not advance) to converge, the trial was closed at the time.

[0025]

[Table 1]

電解液耐電圧試験結果	
実施例1	0. 0 5mF / cm ² 分解後、6. 5 Vまで安定
実施例2	0. 0 3mF / cm ² 分解後、6. 5 Vまで安定
実施例3	0. 0 1mF / cm ² 分解後、6. 5 Vまで安定
比較例1	約5. 0 Vで継続的に分解
比較例2	約4. 6 Vで継続的に分解
比較例3	約4. 7 Vで継続的に分解

	Result of Electrolytic solution withstand voltage test	
Exam. 1	decomposition	0.05 mF/cm ² . ,after then stable to 6.5V
Exam. 2	decomposition	0.03 mF/cm ² . ,after then stable to 6.5V,
Exam. 3	decomposition	0.01 mF/cm ² . ,after then stable to 6.5V,
Comp. 1	Decomposition	continuously at ca.5.0V
Comp. 2	decomposition	continuously at ca.4.6V
Comp. 3	decomposition	continuously at ca.4.7V

[0026] As shown in Table 1, decomposition was settled immediately after that and the electrolytic solution of examples 1-3 was stable after that to 6.5V, although decomposition arose just at first. It decreased even to one fifth in case the total amount of decomposition is an example 1, and stability was excellent in the example 3 which mixed especially trialkyl phosphate. On the other hand, all, decomposition arose continuously less than [5V], and the examples 1-3 of a comparison did not have what is borne to 5.5V.

[0027] The mixture of a graphite and the polyvinylidene fluoride as a binder is used for example 4 negative electrode, and it is LiMn_{1.5} Ni_{0.5}O₄ to a positive electrode. The coin cel was produced using the same thing as the electrolytic solution of an example 3 using mixture with the polyvinylidene fluoride as the scale-like graphite and binder as an electric conduction assistant to the electrolytic solution.

[0028] The coin cel was produced like the example 4 except having used the same thing as the electrolytic solution of the example 2 of a comparison for the example of comparison 4 electrolytic solution.

[0029] It charged to 5.2V about the cell of the above-mentioned example 4 and the example 4 of a comparison, and although discharge capacity was hardly obtained by the cell of the example 4 of a comparison when the discharge capacity at the time of making it discharge to 3.5V was measured, the cell about 50 times the discharge capacity of the example 4 of a comparison was obtained by the cell of an example 4.

CLAIMS

[Claim(s)]

[Claim 1] Nonaqueous electrolyte characterized by containing at least two, the fluorine-containing ether, the partial saturation ether, or partial saturation ester, 5% or more by the volume ratio, respectively.

[Claim 2] Nonaqueous electrolyte which at least two, the fluorine-containing ether, the partial saturation ether, or partial saturation ester, and other electrolytic-solution solvents are contained, and all electrolytic-solution solvents are contained for the above-mentioned fluorine-containing ether, the partial saturation ether, or partial saturation ester 5% or more by the volume ratio, respectively, and is characterized by 85% or more of other electrolytic-solution solvents being solvents more than with stable 5V on trialkyl phosphate and/or a carbon material front face.

[Claim 3] Nonaqueous electrolyte according to claim 1 or 2 characterized by the fluorine-containing ether being the straight chain-like fluorine-containing ether.

[Claim 4] at least one of the straight chain ends of the straight chain-like fluorine-containing ether according to claim 3 -CHF₂ it is -- nonaqueous electrolyte characterized by things.

[Claim 5] Nonaqueous electrolyte according to claim 1 or 2 characterized by the ether or partial saturation ester of partial saturation being vinylene carbonate or its derivative.

[Claim 6] Nonaqueous electrolyte according to claim 2 characterized by including phosphoric-acid trialkyl 10% or more by the volume ratio as trialkyl phosphate.

[Claim 7] The nonaqueous electrolyte rechargeable battery characterized by using nonaqueous electrolyte according to claim 1 to 6.

[Claim 8] The nonaqueous electrolyte rechargeable battery according to claim 7 characterized by the ability of the potential of one [at least] electrode of a positive electrode or a negative electrode to become more than 4.5V on metal lithium criteria.

[Claim 9] The nonaqueous electrolyte rechargeable battery according to claim 7 or 8 characterized by using the graphite ingredient which made amorphous the amorphous carbon ingredient and/or the front face as an electric conduction assistant of a positive electrode.

[Claim 10] The nonaqueous electrolyte rechargeable battery whose peak intensity ratio (I₁₃₆₀/I₁₆₀₀) of 1360cm⁻¹ and 1600cm⁻¹ is 0.4 or more in the Raman spectrum of the graphite ingredient which made amorphous an amorphous carbon ingredient and/or a front face according to claim 9.

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(71)出願人 000005810

日立マクセル株式会社

大阪府茨木市丑寅1丁目1番88号

(72)発明者 篠田 直樹

大阪府茨木市丑寅一丁目1番88号 日立マ
クセル株式会社内

(74)代理人 100078064

弁理士 三輪 鐵雄

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(54)【発明の名称】非水電解液およびそれを用いた非水電解液二次電池

(57)【要約】

【課題】 炭素材料表面で5V以上でも安定な非水電解液を提供し、それによって、少なくとも一方の電極電位がリチウム基準で4.5Vとなり得る非水電解液二次電池を提供する。

【解決手段】 含フッ素エーテル、不飽和エーテルまたは不飽和エステルの少なくとも2つをそれぞれ体積比で5%以上含有させて非水電解液を構成する。また、含フッ素エーテル、不飽和エーテルまたは不飽和エステルの少なくとも2つと、他の電解液溶媒とを含有させ、上記含フッ素エーテル、不飽和エーテルまたは不飽和エステルはそれぞれ体積比で全電解液溶媒の5%以上含有させ、他の電解液溶媒の85%以上はリン酸トリエステルおよび/または炭素材料表面で5V以上でも安定な溶媒を用いて非水電解液を構成する。

【特許請求の範囲】

【請求項1】 含フッ素エーテル、不飽和エーテルまたは不飽和エステルの少なくとも2つがそれぞれ体積比で5%以上含まれていることを特徴とする非水電解液。

【請求項2】 含フッ素エーテル、不飽和エーテルまたは不飽和エステルの少なくとも2つと、他の電解液溶媒とが含まれ、上記含フッ素エーテル、不飽和エーテルまたは不飽和エステルがそれぞれ体積比で全電解液溶媒の5%以上含まれ、他の電解液溶媒の85%以上がリン酸トリエステルおよび／または炭素材料表面で5V以上でも安定な溶媒であることを特徴とする非水電解液。

【請求項3】 含フッ素エーテルが直鎖状含フッ素エーテルであることを特徴とする請求項1または2記載の非水電解液。

【請求項4】 請求項3記載の直鎖状含フッ素エーテルの直鎖末端の少なくとも1つが $-CH_2F$ であることを特徴とする非水電解液。

【請求項5】 不飽和のエーテルまたは不飽和エステルがビニレンカーボネートまたはその誘導体であることを特徴とする請求項1または2記載の非水電解液。

【請求項6】 リン酸トリエステルとしてリン酸トリアルキルを体積比で10%以上含むことを特徴とする請求項2記載の非水電解液。

【請求項7】 請求項1～6のいずれかに記載の非水電解液を用いたことを特徴とする非水電解液二次電池。

【請求項8】 正極または負極の少なくとも一方の電極の電位が金属リチウム基準で4.5V以上となり得ることを特徴とする請求項7記載の非水電解液二次電池。

【請求項9】 正極の導電助剤として、非晶質炭素材料および／または表面を非晶質化した黒鉛材料を用いたことを特徴とする請求項7または8記載の非水電解液二次電池。

【請求項10】 請求項9記載の非晶質炭素材料および／または表面を非晶質化した黒鉛材料のラマンスペクトルにおいて 1360 cm^{-1} と 1600 cm^{-1} のピーク強度比(I_{1360}/I_{1600})が0.4以上である非水電解液二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、非水電解液およびそれを用いた非水電解液二次電池に関し、さらに詳しくは、高電圧に耐え得る非水電解液およびそれを用いて高電圧化し得る非水電解液二次電池に関する。

【0002】

【従来の技術】リチウム二次電池に代表される非水電解液二次電池は、高容量で、かつ高電圧、高エネルギー密度であることから、近年急激に生産が拡大している。

【0003】

【発明が解決しようとする課題】小型携帯機器などの普及につれ、この非水電解液二次電池においても、さらなる高容量化が求められているが、そのための技術の一案として正極活物質を従来の4V級のものから5V級に変え、電池電圧を上げることで電力ベースの容量アップを図ろうとする試みがなされている。

【0004】しかしながら、現在非水電解液二次電池用の非水電解液(以下、電池を表すとき以外は、「電解液」と略す)の溶媒として使用されているもののほとんどは、電池電圧が5V以上になると正極の導電助剤として使用されている黒鉛などの炭素材料表面で酸化分解されてしまう。したがって、5V級の電池の実用化のためには、5V以上でも分解しにくい電解液溶媒を用いることが必要である。

【0005】

【課題を解決するための手段】本発明は、上記課題を解決すべき鋭意検討した結果なされたものであり、電解液溶媒として、含フッ素エーテル、不飽和のエーテルまたは不飽和エステルの少なくとも2つを体積比でそれぞれ5%以上含有させることによって、5V以上でも炭素材料表面でほとんど分解しない、あるいは最初に分解してもすぐに安定化し、それ以後、まったく分解しない電解液が得られることを見出したものである。

【0006】すなわち、本発明者は、含フッ素エーテルと不飽和エーテルまたは不飽和エステルの少なくとも2つがそれぞれ体積比で5%以上含まれる電解液が5V以上の炭素材料表面でも安定して使用できることを見出した。従来の電解液では電圧が5Vまで上昇すると炭素材料表面で継続的に分解を続けるが、本発明の電解液では最初に若干の分解電流が流れるものの、極めて早い段階で分解反応が収束して安定化し、それ以後は少なくとも6.5Vまで分解を起こさない。

【0007】

【発明の実施の形態】本発明において用いる含フッ素エーテルとしては、それ自身の耐酸化性が高いものが好ましく、フッ素化率(水素のフッ素への置換率)が高いほど耐酸化性も高いため、フッ素化率は30%以上が好ましく、55%以上がより好ましい。また、電池特性の面から分子構造は鎖状が好ましく、特に直鎖状が好ましい。さらに、直鎖状の場合は少なくとも1末端は $-CH_2F$ であることが好ましい。含フッ素エーテルの電解液溶媒中での比率は体積比で5%以上が必要であり、充分な効果を得るには10%以上が好ましく、20%以上がより好ましく、30%以上がさらに好ましい。ただし、電池特性の面からは含フッ素エーテルの電解液溶媒中の比率は体積比で80%以下が好ましい。

【0008】不飽和エーテルまたは不飽和エステルとしては、例えば、ビニレンカーボネートおよびその誘導体〔例えば、ジメチル-1,3-ジオキソール-2-オン(dimethyl-1,3-dioxol-2-one)〕が好適なものとして挙げられ、電解液溶媒中の比率は体積比で5%以上が必要であり、充分な効果を得

るには10%以上が好ましい。ただし、電池特性の面からは不飽和エーテルまたは不飽和エステルの電解液溶媒中の比率は体積比で60%以下が好ましく、30%以下がより好ましい。

【0009】さらに、上記二種類の溶媒以外にも任意の溶媒を混合して使用できるが、そのような溶媒中の体積比で85%以上はリン酸トリエステルおよび/または炭素材料表面で5Vでも安定な溶媒でなければならない。上記リン酸トリエステルとしては例えばリン酸トリメチルやリン酸トリエチルなどのリン酸トリアルキルが挙げられる。リン酸トリエステルは、上記二種類の溶媒と混合して用いるとより速やかに安定化するので電解液溶媒中に体積比で5%以上が好ましく、10%以上がより好ましい。ただし、電池特性の面からは上記リン酸トリエステルの電解液溶媒中の比率は体積比で80%以下が好ましく、40%以下がさらに好ましい。また、単独で炭素材料表面で5V以上でも安定な溶媒としては、フッ素化したエーテル類（これは本発明の必須構成溶媒である含フッ素エーテルと同一種でも構わない）、フッ素化したエステル類、フッ素化したカーボネート類などが挙げられる。なお、ここでいう5V以上でも安定とは、本発明の実施例に示したと同様の耐電圧試験において5V以下での分解電気量が電極単位面積当たり0.05mF以下であることを意味し、本発明においては、この条件下で5.5V以上でも安定なものが好ましい。

【0010】電解液の電解質としては、例えば、LiC₁O₄、LiPF₆、LiBF₄、LiAsF₆、LiSbF₆、LiCF₃SO₃、LiC₄F₉SO₃、LiCF₃CO₂、Li₂C₂F₄(SO₃)₂、LiN(CF₃SO₂)₂、LiC(CF₃SO₂)₃、LiC_nF_{2n+1}SO₃(n≥2)、LiN(RfOSO₂)₂〔ここでRfはフルオロアルキル基〕などが単独でまたは2種以上混合して用いられるが、特にLiPF₆や炭素数2以上の有機フッ化物Li塩などが好ましい。電解液中における電解質の濃度は、特に限定されることはなく、濃度を0.6mol/l以上の多めにすると安全性がより向上するので好ましく、0.8mol/l以上がより好ましい。また、2.0mol/lより少ないと粘度が低くなるので好ましい、1.6mol/lより少ないとより好ましい。電解液はこれらの電解質を電解液溶媒中に溶解させることによって調製されるが、電解液中の電解質の体積は極めて小さく、電解液の体積は電解液溶媒の体積と実質的に同一であり、上記含フッ素エーテルや不飽和エーテルまたは不飽和エステル、リン酸トリエステル類などの電解液溶媒中で占める体積は実質上それらが電解液中で占める体積と同一であるとみなすことができる。

【0011】本発明において、正極活物質としては、4.5~6Vで動作するものなら何でも良いが、例えばLiMn₂O₄にNi、Cr、Feなどを置換した5V

系リチウムマンガン酸化物が好適なものとして挙げられる。これらのなかでもNi置換したものがサイクル特性などが優れているので特に好ましい。さらに、正極には導電助剤として通常炭素材料が用いられるが、本発明は、導電助剤の炭素材料上での電解液の分解を抑制するものであることから、導電助剤として炭素材料を使用した正極に適用するとサイクル寿命の向上などに効果が現れる。導電助剤としての炭素材料としては導電性の高い黒鉛材料が好ましいが、黒鉛材料にカーボンブラックなどの低結晶材料を微量併用すると電池特性が向上するので特に好ましい。導電助剤の量としては容量密度を確保するため正極材料（つまり、正極活物質、導電助剤、バインダーなどで構成されるものであって、集電体やタブなどは含まない）中において重量比で20%以下が好ましく、10%以下がさらに好ましいが、導電性を確保するためには5%以上が好ましい。また、上記の黒鉛材料としては、特にCVD（化学気相法）などによって表面を低結晶炭素材料で被覆して非晶質化した黒鉛材料がより速やかに電解液と安定化するので好ましい。このような非晶質化した黒鉛材料ではラマンスペクトルにおいて1360cm⁻¹と1600cm⁻¹のピーク強度比(I₁₃₆₀/I₁₆₀₀)が0.4以上であることが好ましい。

【0012】正極は、例えば、上記正極活物質に、必要に応じて、上記のような導電助剤や例えばポリフッ化ビニリデン、ポリテトラフルオロエチレンなどのバインダーを加え、混合して正極合剤を調製し、それを溶剤で分散させてペーストにし（バインダーはあらかじめ溶剤に溶解させてから正極活物質などと混合してもよい）、その正極合剤含有ペーストを金属箔などからなる正極集電体に塗付し、乾燥、圧縮して、正極集電体の少なくとも一部に正極合剤層を形成することによって作製される。ただし、正極の作製方法は上記例示の方法に限られることなく、他の方法によっててもよい。

【0013】負極に用いる材料としては、リチウムイオンをドープ・脱ドープできるものであればよく、本発明においては、このようなリチウムイオンをドープ・脱ドープできる物質を負極活物質と呼ぶが、このような負極活物質としては例えば、黒鉛、熱分解炭素類、コークス類、ガラス状炭素類、有機高分子化合物の焼成体、メソカーボンマイクロビーズ、炭素繊維、活性炭などの炭素化合物であればよい。また、Si、Sn、Inなどの合金あるいはLiに近い低電位でも充放電できる酸化物などの化合物は炭素材料に比べ高い容量をもつものがあり、それらは負極活物質として好ましい。

【0014】負極は、例えば、上記負極活物質に、必要に応じ、正極の場合と同様の導電助剤やバインダーなどを加え、混合して負極合剤を調製し、それを溶剤に分散させてペーストにし（バインダーはあらかじめ溶剤に溶解させておいてから負極活物質などと混合してもよい）、その負極合剤含有ペーストを銅箔などからなる負

極集電体に塗付し、乾燥、圧縮して、負極集電体の少なくとも一部に負極合剤層を形成することによって作製される。ただし、負極の作製方法は上記例示の方法に限られることなく、他の方法によつてもよい。

【0015】上記正極集電体や負極集電体としては、例えば、アルミニウム、銅、ニッケル、ステンレス鋼などの箔や、それらの金属を網状にしたものなどが用いられるが、正極集電体としては特にアルミニウム箔が適しており、負極集電体としては特に銅箔が適している。

【0016】セパレータとしては、特に限定されることはないが、強度が充分でしかも電解液を多く保持できるものが好ましく、そのような観点から、厚みが10～50 μm で開孔率が30～70%のポリエチレン製、ポリプロピレン製、エチレンとプロピレンとのコポリマー製の微孔性フィルムや不織布などが好ましい。

【実施例】つぎに、実施例を挙げて本発明をより具体的に説明する。ただし、本発明はそれらの実施例のみに限定されるものではない。

【0017】実施例1

含フッ素エーテルとしての1, 1, 2, 2-テトラフルオロエチル-2, 2, 3, 3-テトラフルオロプロピルエーテル($\text{HCF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$)と、不飽和のエーテルまたはエステルとしてのジメチル-1, 3-ジオキソール-2-オンと、リン酸トリエステルとしてのリン酸トリメチルとを体積比6:3:1で混合した溶媒を電解液溶媒として用いた以外は、実施例1と同様にしてテストセルを組み立てた。

【0018】これとは別に、鱗片状黒鉛〔ラマンスペクトルにおいて 1360cm^{-1} と 1600cm^{-1} のピーク強度比(I_{1360}/I_{1600})=0.1以下の鱗片状黒鉛〕とポリフッ化ビニリデンをN-メチルピロリドンに溶解させた溶液とを混合してペーストを調製した。この合剤ペーストを厚さ20 μm のアルミニウム箔からなる正極集電体の片面に均一に塗付して乾燥し、ローラープレス機により圧縮成形した後、1cm×1cm角に切断し、その正極集電体にリード体を溶接して、耐電圧試験用の試験極を作製した。この試験極と、リチウムフォイルの対極を用い、上記特定の電解液を4ml注入してテストセルを組み立てた。

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*【0019】実施例2

実施例1における鱗片状黒鉛に代えて、CVD法で表面を非晶質化した鱗片状黒鉛〔ラマンスペクトルにおいて 1360cm^{-1} と 1600cm^{-1} のピーク強度比(I_{1360}/I_{1600})=0.6の鱗片状黒鉛〕を用いた以外は、実施例1と同様にしてテストセルを組み立てた。

【0020】実施例3

含フッ素エーテルとしての1, 1, 2, 2-テトラフルオロエチル-2, 2, 3, 3-テトラフルオロプロピル

10 エーテル($\text{HCF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$)と、不飽和のエーテルまたはエステルとしてのジメチル-1, 3-ジオキソール-2-オンと、リン酸トリエステルとしてのリン酸トリメチルとを体積比6:3:1で混合した溶媒を電解液溶媒として用いた以外は、実施例1と同様にしてテストセルを組み立てた。

【0021】比較例1

プロピレンカーボネート100%を電解液溶媒として用いた以外は、実施例1と同様にしてテストセルを組み立てた。

20 【0022】比較例2

ビニレンカーボネート100%を電解液溶媒として用いた以外は、実施例1と同様にしてテストセルを組み立てた。

【0023】比較例3

1, 1, 2, 2-テトラフルオロエチル-2, 2, 3, 3-テトラフルオロプロピルエーテルとプロピレンカーボネートとビニレンカーボネートとの体積比6:3:1の混合溶媒を電解液溶媒として用いた以外は、実施例1と同様にしてテストセルを組み立てた。

30 【0024】〔電解液耐電圧試験〕上記実施例1～3および比較例1～3のテストセルに50 μA の定電流で6.5Vまで電圧を印可して電解液の分解量を調べた。6.5Vに至る前に分解が始まり、分解による消費電気量が 0.15mF/cm^2 に達しても収束する(すなわち、分解が進行しなくなる)兆しがない場合はその時点で試験を打ち切った。

【0025】

【表1】

電解液耐電圧試験結果	
実施例1	0.05mF/cm ² 分解後、6.5Vまで安定
実施例2	0.03mF/cm ² 分解後、6.5Vまで安定
実施例3	0.01mF/cm ² 分解後、6.5Vまで安定
比較例1	約5.0Vで継続的に分解
比較例2	約4.6Vで継続的に分解
比較例3	約4.7Vで継続的に分解

【0026】表1に示すように、実施例1～3の電解液

50 は、最初こそ分解が生じるもの、その後すぐに分解が

収まり、以後6.5Vまで安定であった。特にリン酸トリエステルを混合した実施例3では総分解量が実施例1の場合の1/5にまで減少して安定性が優れていた。これに対して、比較例1~3は、いずれも5V以下で継続的に分解が生じ、5.5Vまで耐えるものがなかった。

【0027】実施例4

負極に黒鉛とバインダーとしてのポリフッ化ビニリデンとの混合物を用い、正極にLiMn_{1.5}Ni_{0.5}O₄と導電助剤としての鱗片状黒鉛とバインダーとしてのポリフッ化ビニリデンとの混合物を用い、電解液に実施例3の電解液と同様のものを用いてコインセルを作製した。

【0028】比較例4

電解液に比較例2の電解液と同様のものを用いた以外

は、実施例4と同様にしてコインセルを作製した。

【0029】上記実施例4および比較例4の電池について5.2Vまで充電し、3.5Vまで放電させたときの放電容量を測定したところ、比較例4の電池ではほとんど放電容量が得られなかつたが、実施例4の電池で比較例4の電池の約50倍の放電容量が得られた。

【0030】

【発明の効果】以上説明したように、本発明では、炭素材料表面で5V以上でも安定な非水電解液を提供することができ、それによって、少なくとも一方の電極電位がリチウム基準で4.5Vとなり得る非水電解液二次電池を提供することができるようになった。